

Volumetric Determination of Small Amounts of Soluble Sulfates

C. L. OGG, C. O. WILLITS, AND F. J. COOPER, *Eastern Regional Research Laboratory, Philadelphia 18, Pa.*

A new technique is described for the volumetric determination of sulfur, in which standard barium chloride is used with the indicators dipotassium rhodizonate or tetrahydroxyquinone. The technique permits continuous following of the colors developed, so that the true end point is easily identified. This makes the titration readily reproducible and results in an appreciable gain in accuracy. The barium chloride solution is standardized, and samples are titrated by the same procedure, eliminating a titration correction factor.

THE volumetric method for determination of sulfur as sulfate with barium chloride, in which the internal indicator tetrahydroxyquinone disodium salt (THQ) or the dipotassium or disodium rhodizonate is used, has been described by a number of investigators (1-12), each of whom has attempted to present a method whereby a sharp or reproducible end point may be obtained. Although satisfactory in the hands of skilled technicians, these methods have not been generally accepted because of difficulty in identifying the true end point. In the titration of sulfate ions with barium chloride, the indicator changes the color of the solution from yellow to orange red. As the end point is approached, but before it is reached, there is a localized formation of the red barium salt of the indicator, which is dispersed through the solution by stirring. This produces a pseudo end point, which slowly disappears as the barium associated with the indicator reacts with remaining sulfate ions. Because of the low concentration of sulfate ions, the reaction becomes very slow as the end point is approached. Unlike most reactions, the true end point is not indicated by a sudden change in color but instead is that point where no fading of the barium-indicator color (orange red) occurs.

The success of the titration depends upon the ability of the analyst to distinguish that point in the titration at which fading no longer occurs. Throughout the titration, there is a slight but gradual change in the stable color from yellow to orange red. As the equivalence point is passed, there is a shift in the color from orange to red, the same as that which occurs with the premature or pseudo end points but distinguishable from them because it is nonfading. If the end point is passed and the titration is continued, the shift in color toward the red is more rapid than that before the end point is reached, and will continue until sufficient barium has been added to combine with the indicator present.

The end point should be easily recognizable if it can be compared with a standard which has the same orange-red hue as the solution which has been titrated just past the equivalence point. However, the fading of the color must be followed continuously to avoid selection of a pseudo end point.

An apparatus and titration technique have been developed which not only identify the end-point color but permit the continuous comparison of the color of the solution with a standard color filter.

The apparatus (Figure 1), consists of a rectangular titration vessel (25 × 45 × 50 mm. high optical absorption cell), a standard 25 × 45 mm. glass color filter, two 5-ml. burets graduated to 0.01 ml., and a titration stand. The titration vessel and the light filter are mounted side by side on an opal glass plate. Illumination is from below, preferably by fluorescent light. All the opal glass is masked except that covered by the titration vessel and the color filter. Best results are obtained when no overhead artificial illumination is used.

PROCEDURE

Sulfate solutions high in carbonates are acidified with nitric acid and boiled. All solutions, either acidic or basic, are neutralized to pH 6.5 to 7.5, the neutral solution is transferred to the titration vessel, and the volume is adjusted to approximately 15 ml. About 0.08 gram of the commercial tetrahydroxyquinone indicator is added and dissolved, and the solution is diluted with an equal volume of 95% ethanol. The solution is titrated with standard barium chloride until the permanent color matches the color filter. At the end point, stirring must be continued long enough (1 to 2 minutes) to make sure that no fading of the orange-red color will occur. A rubber-tipped stirrer is used to prevent scratching the bottom of the absorption cell. The end point is reached when one additional drop of barium chloride causes the solution to appear a deeper red than the color filter. The 0.02 N barium chloride is standardized against a solution containing 1.8140 grams of reagent grade potassium

sulfate per liter of solution. Standardization of the barium chloride in this manner instead of gravimetrically as barium sulfate eliminates a correction factor such as used by Sundberg and Royer (11).

In the titration of a sample for soluble sulfate, unless at least 3 ml. of 0.02 *N* barium chloride are consumed, the assumed normality will be too high, as shown in Figure 2. In the standardization of the barium chloride, unless 3 ml. or more are used, the apparent normality will show rapid changes with correspondingly slight changes in volume of barium chloride. Only when the amount of 0.02 *N* barium chloride required by the sulfate is 3 ml. or more does the normality remain nearly constant. To avoid possible errors through use of an incorrect titer, all titrations, whether standardization or analysis of a sample, should use 3 ml. or more of the 0.02 *N* barium chloride.

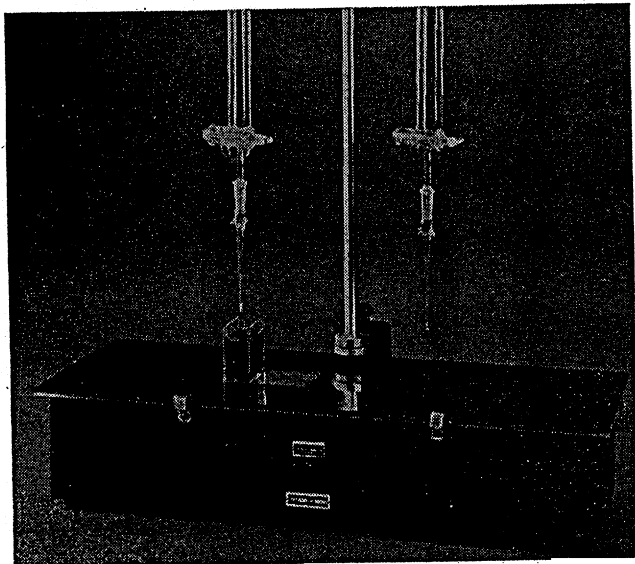


Figure 1. Sulfur Titration Apparatus

In the analysis of microsamples, the amount of sulfur is often so small that less than 3 ml. of the 0.02 *N* standard barium chloride solution will be required. Therefore, when the end point is reached, additional sulfate as standard potassium sulfate is added to bring the volume of barium chloride required to more than 3 ml., and the titration is continued to the second point. Correction is made for the amount of sulfate added. The amount of standard potassium sulfate added can be measured with greater accuracy than the true titer of less than 3 ml. of barium chloride can be determined from a normality curve, and recourse to the curve is eliminated.

Others (2, 5, 11) have noticed this apparent change in titer when small concentrations of sulfur as sulfate are titrated and (2, 5) have attempted to overcome it by using a correction factor. However, the curve shows that when the total volumes of the standard barium chloride solution are small the change in the apparent normality is rapid with correspondingly small change in volume of the barium solution used. Therefore, titrations in which volumes of standard barium chloride less than 3 ml. are used are subject to error.

The standard color filters of polished glass with 37% spectral transmission at $550 \pm 2 \text{ m}\mu$ need not all be identical, if the same filter is used for both the standardization and subsequent titrations of sulfate samples. To compensate for turbidity caused by formation of insoluble white barium sulfate during the titration of samples containing large amounts of sulfur, the polished color filter can be covered by a microscope slide having an appropriately ground surface. It is desirable to have several such slides, each ground to produce a different amount of diffused light. Thus an exact match or compensation of the turbidity of the solution can be made through the selection of the appropriate slide. The slides are easily prepared by grinding with a water suspension of fine Carborundum.

With the apparatus described and the recommended technique, the values obtained on a series of titrations of equal ali-

Table I. Reproducibility of Titration and Determination of Sulfur in Pure Organic Compounds

| A. Agreement Obtained by Analysts | | | |
|---|-----------------------------|--|-----------------|
| Analyst | Sulfur Taken Mg. per ml. | Sulfur Found Mg. per ml. | |
| MJW | 0.333 | 0.333 | |
| | | 0.332 | |
| | | 0.333 | |
| | | 0.334 | |
| CLO | | 0.333 | |
| | | 0.332 | |
| FJC | | 0.334 | |
| | | 0.333 | |
| | | 0.334 | |
| RWB | | 0.334 | |
| | | 0.334 | |
| | | 0.334 | |
| B. Analyses of Pure Organic Compounds | | | |
| Name | Theory % | Found % | Difference % |
| S-Benzyl thiuronium chloride (benzyl isothiurea hydrochloride), Beazley combustion apparatus | 15.82 | <div>15.77</div> <div>15.76</div> <div>Av. 15.77</div> | 0.05 |
| Grote combustion apparatus | 15.82 | <div>15.79</div> <div>15.85</div> <div>Av. 15.82</div> | 0.00 |
| p-Dichlorophenyl sulfone, Beazley combustion apparatus | 11.16 | <div>11.07</div> <div>11.05</div> <div>Av. 11.06</div> | 0.10 |

quots of a sulfate solution varied by not more than ± 0.02 ml. from the mean and the average deviation was 0.01 ml., or 0.003 mg. of sulfur. Table I gives the sulfur values obtained by several analysts for 3 ml. of solution containing 0.333 mg. of sulfur per ml. Two of the four analysts were without experience in this titration. The data show that the reproducibility of results is practically independent of the skill of the analysts. Table I also shows typical analyses obtained on pure organic compounds, the sulfur of which had been converted to sulfate by catalytic combustion.

This paper was suggested by numerous microchemists visiting this laboratory, who had been unsuccessful in the use of the indicators tetrahydroxyquinone or dipotassium rhodizonate for the volumetric determination of soluble sulfates but were able to perform the titration successfully after one demonstration of the procedure described here. They attributed the success of this procedure to the fact that the true end point was easily observed, since the fading of the pseudo end point color could be continuously and accurately followed.

LITERATURE CITED

- (1) Alicino, J. F., *ANAL. CHEM.*, 20, 85 (1948).
- (2) Hallett, L. T., and Kuipers, J. W., *IND. ENG. CHEM., ANAL. ED.*, 12, 360 (1940).

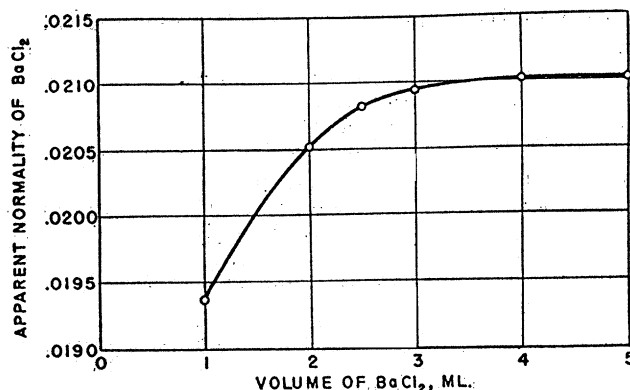


Figure 2. Normality Curve for Barium Chloride, Standardized against 0.0200 *N* Potassium Sulfate.

- (3) Jones, J. H., *J. Assoc. Official Agr. Chem.*, 26, 182-6 (1943).
(4) Lee, S. W., Wallace, J. H., Jr., Hand, W. C., and Hannay, N. B.,
IND. ENG. CHEM., ANAL. ED., 14, 839 (1942).
(5) Mahoney, J. F., and Michell, J. H., *Ibid.*, 14, 97-8 (1942).
(6) Manoy, G. G., and Kirk, P. L., *Ibid.*, 9, 198 (1937).
(7) Schroeder, W. C., *Ibid.*, 5, 403 (1933).
(8) Sheen, R. T., and Kahler, H. L., *Ibid.*, 8, 127 (1936).

- (9) *Ibid.*, 10, 206 (1938).
(10) Sheen, R. T., Kahler, H. L., and Cline, D. C., *Ibid.*, 9, 69 (1937).
(11) Sundberg, O. E., and Royer, G. L., *Ibid.*, 18, 719 (1946).
(12) Wilson, C. W., and Kemper, W. A., *Ibid.*, 10, 418 (1938).